Journal of Materials and Environmental Science
ISSN : 2028-2508
e-ISSN : 2737-890X
CODEN : JMESCN

University of Mohammed Premier Oujda Morocco

J. Mater. Environ. Sci., 2022, Volume 13, Issue 02, Page 139-150

http://www.jmaterenvironsci.com

Employing thermodynamic equilibrium to assess multi-influence between metals treated using photo-electrochemical process

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Received 09 Dec 2021,
Revised 31 Jan 2022,
Accepted 01 Feb 2022

Keywords
- ✓ *Correlation Fuel,*
- ✓ *HSC Chemistry,*
- ✓ *Photo electrochemical,*
- ✓ *Redox potential,*
- ✓ *Runoff*

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Abstract

Photo-electrochemical process (PEC) using anode titanium oxide (TiO_2/UV) was investigated to treat Tehran runoff. Iron (Fe), manganese (Mn), lead (Pb), and zinc (Zn), which are abundant in runoff, were chosen to be analyzed. A new method for employing HSC software was suggested for discovering the effect of the existing metals in untreated runoff on removing each metal by PEC treatment. Application of this method detected that the presence of Zn in runoff samples affected the PEC removal of Fe. According to the Eh/pH diagrams, the species of $ZnFe_2O_4$ showed when Zn in untreated runoff increased, the removal of Fe also increased. The PEC removal of Mn and Pb was not affected by the existence of other metals in untreated runoff. The residual concentrations of Mn were found to be an important factor for predicting the residual concentrations of chemical oxygen demand (COD) in the anaerobic conditions. Regarding correlation matrixes and regression results, dissolved oxygen (DO)-redox potential (Eh), total dissolved solids (TDS)-electrical conductivity (EC), Mn-Fe, Pb-Fe, and Pb-Mn in the aerobic, and TDS-EC, DO-Eh, and Pb-Fe in the anaerobic conditions showed high correlations. EC had the highest contribution to TDS (99.70 and 99.74%) in aerobic and anaerobic conditions. This study can be proposed for evaluating the treatment process of systems containing different metals and better managing the runoff source in Tehran in a cost-efficient manner.

1. Introduction

Runoff is regarded as a significant source for human uses, therefore, it is a seductive option for investigation. Its quality could be seriously affected by metals or organic compounds, thus, must be treated. Realizing transport mechanisms and speciation of metals is significant for improving the management strategies and enhancing the runoff quality [1]. Photo-assisted electrochemical (PEC) process has received considerable attraction in order to further accelerate the photo-catalysis (PC) reaction. Applying an anodic potential improves the charge carrier (electron/hole) separation and withdraws electrons from the photo-anode to a cathode. This way can prevent the recombination of charge carriers and prolong the hole's lifetime, which means a better catalytic activity. Oxidation on the hole and reduction by electrons occur on the surface of the anode and cathode, respectively [2].

The control of Eh and pH can play a crucial role during the PEC process. This is recognized by influencing the reactions on the electrodes and the oxidation states and solubility of metals [3]. Although the thermodynamic significance of Eh has been unbelieved, testing systems under a range of Eh levels can assist in better realizing the fate, pathway, toxicity, and solubility of metals in the environment [4]. Employing Eh/pH diagrams can explain the form of metals after treatment, the changes that occurred on them, and the mechanisms (oxidation, reduction, adsorption, etc.) of the PEC process [5].

Recently, it is found that the toxicity of one metal could become more acute when it co-exists with other metals [6]. The presence of more than one metal in the water system often causes correlations and mutual influence between them and has to be considered [7].

Many investigators have focused on speciation studies for assessing the risk of metals (individually). For instance, E.T. Wahyuni et al. [5], employed speciation and Eh/pH diagrams to explain the mechanisms (oxidation, reduction, adsorption) of the PC process for removing copper (Cu), cadmium (Cd), chromium (Cr), and Pb from solution. Also, it assessed the mutual effect of Cd, Cr, and Pb on Cu removal by costly laboratory analysis. Yahya *et al.* [8], applied HSC software and Eh/pH diagrams for assessing the stability of Neodymium (Nd), Cerium (Ce), and Lanthanum (La). The results showed that these elements follow the stability order: Ce > Nd > La. Furthermore, D. ALabdeh et al. [9], investigated the speciation of several metals using Eh/pH diagrams in Anzali Wetland. They concluded that Arsenic (As), Cd, Cr, and Fe existed in very toxic forms.

To date, there has been no investigation on providing a cost-efficient and theoretical insight into the speciation of metals (Fe, Mn, Pb, and Zn) after treatment considering the mutual effect of metals on each other, Hence, the importance of the current study is clear in providing a comprehensive and time-saving *technique* of the speciation by using the least number of chemical analyses.

In recent years, statistical methods such as correlation and regression analysis have been comprehensively utilized as analytical tools for rapid predicting and monitoring of the quality parameters or the concentration of pollutants in water [10]. Correlation analysis is a standard regression type parameter and assigned as a measure of the existence of the predictable linear correlation between the analyzed and predicted variables [11]. As the chemical analysis demands a long time and a high cost, regression would be an appealing solution to estimate relationships between several parameters and an easily measurable parameter [12].

Understanding the statistical relationships between parameters and multiple metals can supply comprehend insight on tracking the transport of these metals and ascertaining treated runoff quality in a cost-efficient manner [1].

For the first time, the objective of this work was to evaluate the relationship and mutual effect between the studied metals by drawing new Eh/pH diagrams without using expensive laboratory devices and to estimate the impact of the residual metals on the residual COD in the treated runoff via calculating multiple regression equation. Also, it aimed to select the most influential variables controlling metal contents and other parameters, to predict the concentrations of metals and parameters in the treated runoff with acceptable accuracy via calculating linear regression equations in a cost-efficient manner, and to calculate the percentage contribution of each variable in predicting metal contents or quality parameters. The current research is unique in that it estimates relationships between quality parameters and multiple metals in runoff after PEC treatment (not in raw runoff).

2. Methodology

2.1 Experiments

Runoff samples were collected in 2020 during three months from Kan canal, located in the south of Tehran, which was one of the most contaminated regions of Tehran. The samples were analyzed before the PEC experiments to obtain their Eh, pH, DO, TDS, EC, COD, and concentrations of metals, while the residual samples were employed for more research and treatment. The PEC reactor (2L) contained one photo-anode (Ti/TiO_2) and one cathode (Graphite). The photo-anode was irradiated by a UVA source (8W, 380 nm). Four sets of experiments were achieved. Each of the first and third sets consisted of six tests to determine the effect of anodic bias potential (5.5 and 10 V) and gaps between the electrodes (6-10-12 cm), and the effect of gaps and high Eh > +164 mV and low Eh < +100 mV, respectively. Each of the second and fourth sets also consisted of six tests to evaluate the influence of anodic bias potential and concentrations of NaCl electrolyte (0.4 - 0.65 - 1 g/L), and the influence of NaCl and high and low Eh, respectively. Eh increased by increasing the anodic potential and decreased by adding a reducing agent (Sodium ascorbate). Every experiment was repeated 2 times for ensuring the reliability.

2.2 Analytical techniques and data

At the sample site, Eh and pH were measured using a portable multi-parameter probe. Metals' concentrations were analyzed by inductively coupled plasma-mass spectrometry. COD, which is a typical mineralization index of organic compounds, was employed as a probe compound and measured by a spectrophotometer (*DR 5000*- Hach). For obtaining the Eh/pH diagrams by HSC, distinct parameters such as pH, temperature, Eh, pressure, and concentration of the metal were needed.

The current study had applied the linear and multiple regression analysis to define relationships between quality parameters and metals, as well as between COD and metals after PEC treatment. For this purpose, different linear regression equations were formulated taking several runoff quality parameters as independent variables and metals as dependent variables. In multiple regression, metals and COD were considered as independent and dependent variables, respectively. The correlation matrixes of five parameters and four metals were formulated and showed in **Table 2**. A high and positive correlation coefficient (r nearly 1) indicated that the relationship between the two variables was strong. While negative values of correlation coefficient (r nearly -1) revealed an inverse relationship. If the *p*-value was statistically significant at $p \leq 0.05$, the interaction term would be definitely important in the model, but if this outcome was not obtained, the interaction term could be removed from the regression model [13].

3. Results and Discussion

3.1 Method development

In the current study, a new method was proposed and it used HSC for defining the correlation between metals and its influence on their removal by PEC purification. New Eh/pH diagrams by entering data related to all metals at the same time were drawn. Instead of putting the data of only one metal in the two distinct columns [14], the studied metal and its molality (after treatment) were put in the column of "select main element" and the other measured metals (which their effect on the studied metal's removal has to be studied) and their molality (after treatment) were arranged in the column of "select other metals". These diagrams reflected the correlation of each metal and its removal affected by the presence of other metals. Speciation of each metal based on the existence of other metals and its effect on the metal removal

Figure 1 shows the speciation of each metal according to the existence of all the studied metals together in Tehran runoff after treatment with high Eh conditions (in its left part) and after the treatment with low Eh conditions (in its right part). The dominant species of Fe under high Eh were Fe_2O_3 and $ZnFe_2O_4$ (the valence of Fe is +3), and they were Fe (+2a), Fe_2O_3, and $ZnFe_2O_4$ under anaerobic conditions (**Figures 1a-b**). The dominant species of Zn under high Eh were Zn (+2a) and $ZnFe_2O_4$, and they were Zn (+2a) and $ZnFe_2O_4$ under low Eh (**Figures 1g -h**).

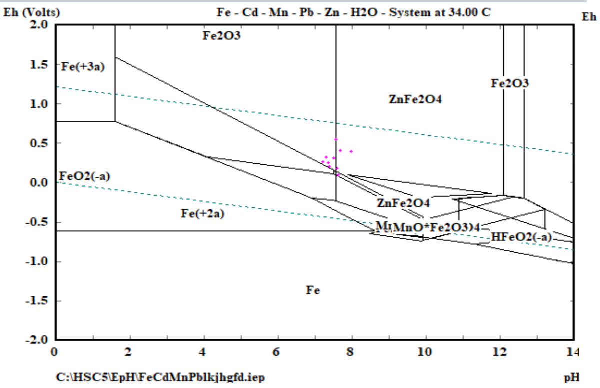

Figure 1a. Speciation of Fe in high Eh

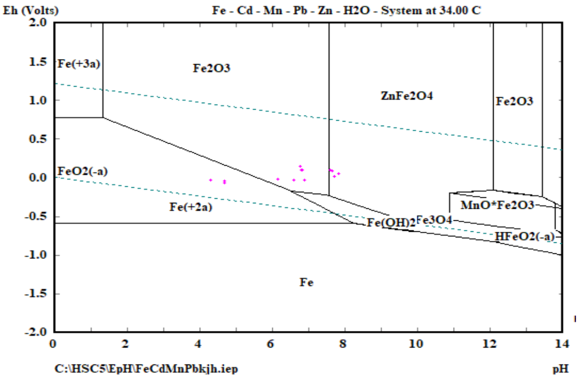

Figure 1b. Speciation of Fe in low Eh

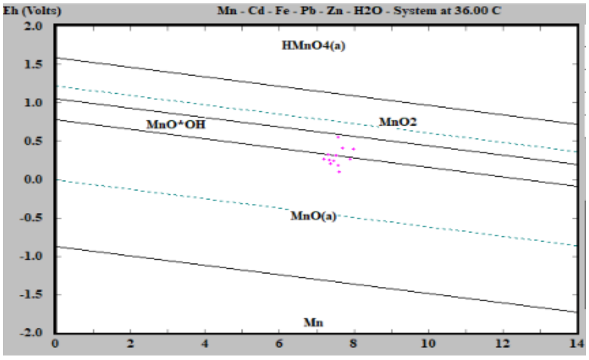

Figure 1c. Speciation of Mn in high Eh

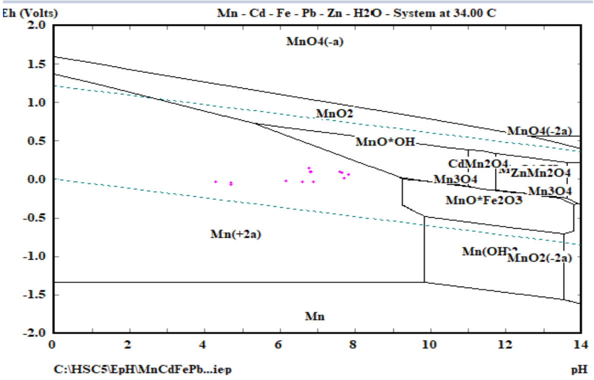

Figure 1d. Speciation of Mn in low Eh

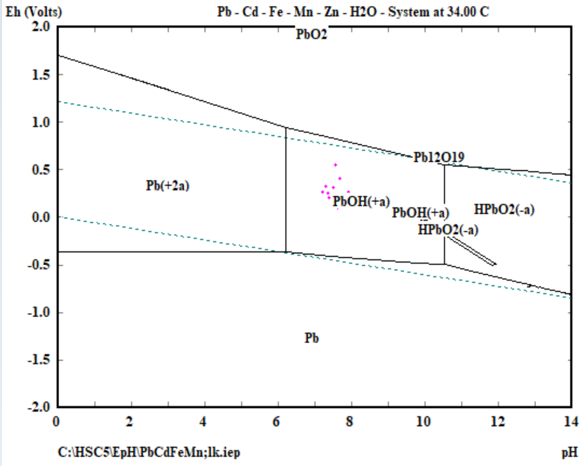

Figure 1e. Speciation of Pb in high Eh

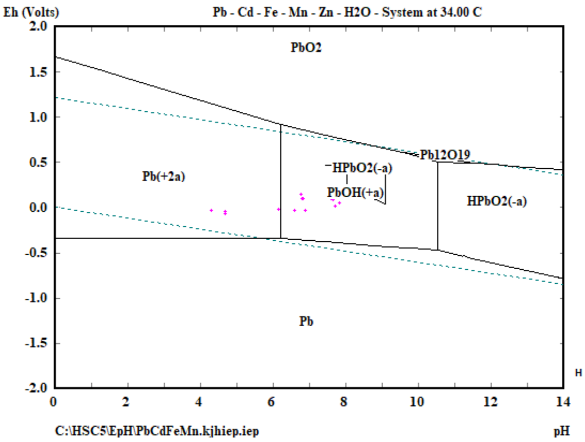

Figure 1f. Speciation of Pb in low Eh

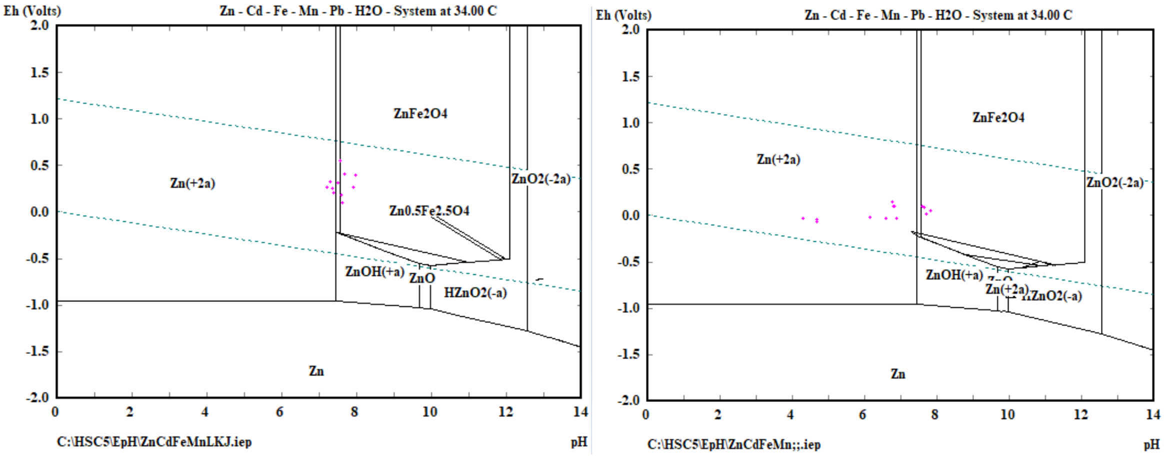

Figure 1g. Speciation of Zn in high Eh

Figure 1 h. Speciation of Zn in low Eh

Figure 1. Speciation of Fe, Mn, Pb, and Zn in Tehran runoff under the multi-influence of the existence of other metals after the PEC process (the left diagrams during high Eh and the right diagrams during low Eh).

This referred to the existence of a relationship between the concentrations of Fe and Zn in the untreated runoff by staying Zn^{+2} in runoff (before and after treatment) and oxidizing Fe^{+2} to Fe^{+3} and precipitating it according to all the experiments and sets after treatment. Zn had an effect on the concentrations and effectiveness of removing Fe and the two metal might have similar precipitation attitudes. When Zn concentrations in raw runoff increased, the removal of Fe by PEC oxidation increased and the residual of Fe decreased. Increased Zn releasing during the aerobic condition (high Eh) leads to an increase in its concentration [15]. This phenomenon was in disagreement with the finding by J. Boccio et al. [16] who observed the negative effect of Zn on Fe absorption in water. Mn species according to the presence of other metals under high Eh were MnO_2, MnO*OH, and MnO(a); it was Mn(+2a) under low Eh (**Figures 1c-d**). No metals in the untreated runoff affect the concentration of Mn after the treatment. This finding was in agreement with the report by H.H. Oyem et al. [17] who revealed no significant relationship between Mn and other studied metals (Fe and Zn). The prevalent Pb species after the PEC process under high Eh were Pb(OH)(+a) and were Pb(OH)(+a) and Pb(+2a) under low Eh (**Figures 1e-f**). This meant that Pb removal, similar to Mn, was not affected by the presence of other metals in the untreated Tehran runoff. This result was in disagreement with the research performed by M.A. Agoro et al. [18], which reported the existence of a positive relationship and similar accumulation behaviors between Pb and Zn in the wastewater and river water samples. Also, this result did not match the one obtained by F.M. Pang et al. [6]. They revealed that the removal effectiveness of Pb had a negative correlation with Zn and a positive correlation with Fe.

3.2 Relationship between the organic compounds and metals in trated runoff

Table 1 presents the descriptive statistics of the variables in all sets of PEC treatment using different experimental parameters and presents the coefficients of multiple regression during two cases of Eh in treated runoff. By conducting multiple regression analysis with Excel 2013, the relationship and equation between COD and studied metals for every two sets and each case of Eh was determined. As shown in **Table 1**, in the case of high and low Eh, R^2 = 0.66 and 0.88 referred that 66% and 88% of the variance in the residual COD could be explained by the residual metals after the PEC process, respectively. The regression model for case 1 was given as: COD (mg/L) = 14.5539 + 0.0048 Fe –

0.0806 Mn + 3.9608 Pb + 0.1515 Zn, and for case 2 was given as: COD (mg/L) = 14.1482 + 0.0017 Fe + 0.0239 Mn + 0.3720 Pb + 0.0055 Zn. According to analysis of variance, it could be found that the significance values of F in cases 1 and 2 were 0.073 ($p > 0.05$) and 0.002 ($p < 0.05$), respectively. These findings indicated that the model for case 2 was an important predictor of the performance of COD. To reveal the contribution of each variable (metal) to the predictive models, significance coefficient of t-state for each metal was assessed. These coefficients in cases 1 and 2 for Fe, Mn, Pb, and Zn were 0.22, 0.44, 0.26, 0.53 and 0.29, 0.05, 0.52, 0.96, respectively. It can be seen that no metals in the model of case 1 ($p > 0.05$) significantly contributed to the model, but in case 2, Mn was the only contributor to this model, i.e. 0.05 ($p \leq 0.05$). This finding indicated that, in the third and fourth sets, Mn was the important metal that influenced the oxidation of organic compounds by PEC and suggested a dominance of Mn in the control of COD. As a result, the linear regression between COD and Mn must be calculated. Here, the significance value of F was 0.014 ($p < 0.05$); also, the significance value of t-state was 0.014 ($p < 0.05$). The percentage contribution of Mn to COD was 46%. The prediction of the residual concentrations of COD can be achieved by measuring the residual concentrations of Mn using the following equation:

$$Y_{(\text{the residual of COD after PEC})} = 25.7528 + 0.0449\, X_{(\text{the residual of Mn after PEC})} \qquad \textbf{Eqn. 1}$$

Accordion to equation (1), for each unit increase in the residual of Mn, the residual of COD increased at least 0.0449 in the treated runoff during anaerobic conditions. By applying equation (1), the cost needed for COD measurement after PEC was avoided.

Table 1. Descriptive statistics of the variables and coefficients of multiple regression in runoff after PEC treatment

Set	Test	Case of Eh	Value	Eh, mV	COD, mg/L	Fe, µg/L	Mn, µg/L	Pb, µg/L	Zn, µg/L	R^2	Sig.of F
1 st set	Test 1	1- High Eh	Mean	254	37	1643	75	3	35	0.66	0.073
			Minimum	244	30	640	41.6	2.4	22.7		
			Maximum	263	46	3550	140	4.4	46.7		
			*SD	9.6	8.2	1652	56.4	1	12		
	Test 2		Mean	306	29	263	39	2	43		
			Minimum	270	25	20	30	1.33	27.9		
			Maximum	329	32	550	50	3.2	52.2		
			SD	31.7	3.5	267.6	10.1	0.9	13		
2 st set	Test 1		Mean	164	30	2603	207	5	16		
			Minimum	98	10	410	100	3.1	10.3		
			Maximum	211	48	6850	370	7.3	21.4		
			SD	58.6	19	3678.3	143.6	2.1	5.5		
	Test 2		Mean	453	21	87	71	2	20		
			Minimum	396	8	50	60	1.2	10.7		
			Maximum	550	33	140	90	2.1	35.8		
			SD	84.6	12.5	47.2	16.2	0.4	14.1		

Sig. of t For Case 1						0.22	0.44	0.26	0.53	0.66	0.073
3 st set	Test 1	2-Low Eh	Mean	116	40	5985	383	25	35	0.88	0.002
			Minimum	96	35	3794	320	19.2	22		
			Maximum	152	45	10171	440	32.5	47.6		
			SD	31.5	5	3626.5	60.2	6.7	12.7		
	Test 2		Mean	-48	64	10867	550	35	20		
			Minimum	-65	62	9635	460	31.9	8.08		
			Maximum	-35	67	11581	610	37.6	28.9		
			SD	15.3	2.6	1071.6	79.3	3	10.8		
4 st set	Test 1		Mean	68	42	5048	513	18	42		
			Minimum	20	33	3299	460	13	30.1		
			Maximum	97	52	8084	600	24.5	53.2		
			SD	42	9.5	2639.6	75.7	5.9	11.5		
	Test 2		Mean	-27	60	8349	843	30	16		
			Minimum	-33	52	5750	780	19.6	5.6		
			Maximum	-20	65	9753	910	36	36.4		
			SD	6.5	6.8	2253.4	65	8.9	17.7		
Sig. of t For Case 2						0.29	0.05	0.52	0.96	0.88	0.002

*SD: Standard Deviation.

3.3 Correlation and linear regression analysis

The correlation matrixes for different runoff quality parameters and metals treated during high and low Eh conditions are showed in **Table 2**. During high Eh treatment, the matrix indicated that pH had a positive correlation with Eh, DO, EC, TDS, Mn; negative correlation with Fe, Pb, and Zn. Eh showed a positive correlation with DO, Zn; weak correlation with EC, TDS; negative correlation with Fe, Mn, Pb. This finding was in agreement with our previous result. It had revealed that the removal rate of Fe, Mn, and Pb by oxidation was increased and the removal rate of Zn was decreased during Eh increasing [19], but this finding was in disagreement with the result obtained by M. Kang et al. [20] who demonstrated that Zn was released and its concentration was increased in anoxic and low Eh conditions. DO had a positive correlation with Zn; weak correlation with EC, TDS; negative correlation with Fe, Mn, Pb. EC showed a positive correlation with TDS, Fe, Mn, Pb; negative correlation with Zn. TDS had a positive correlation with Fe, Mn, Pb; negative correlation with Zn. Fe had a positive correlation with Mn, Pb; negative correlation with Zn. Mn had a positive and a negative correlation with Pb and Zn, respectively. Pb had a negative correlation with Zn. According to the matrix during low Eh treatment, pH had a positive correlation with Eh, DO, EC, TDS, Zn. While, a negative correlation coefficient among pH and Fe, Mn, Pb was seen. Eh had a positive correlation with DO, Zn; negative correlation with EC, TDS, Fe, Mn, Pb. DO had a positive correlation with Zn; negative correlation with EC, TDS, Fe, Mn, Pb. EC had a positive correlation with TDS, Mn, Zn; negative correlation with Fe, Pb. TDS had a positive correlation with Mn, Zn, while a negative correlation with Fe, Pb. Fe had a positive correlation with Mn, Pb; negative correlation with Zn. Mn had a positive and a negative correlation with Pb and Zn, respectively.

It can be concluded that Eh, pH, and EC were important physicochemical parameters of runoff during the two cases of treatment because they were associated with most of the examined variables in the current study. The regression models had only considered parameters and metals having correlation coefficients greater than 0.5 according to the information shown in **Table 2**. The systematic computation of regression equations supplied indirect means for the fast assessment of runoff quality and its content of metals after PEC treatment.

Table 2. Correlation matrixes for quality parameters and metals after PEC treatment of Tehran runoff during high and low Eh

Zn, µg/L	Pb, µg/L	Mn, µg/L	Fe, µg/L	TDS, mg/L	EC, µs/cm	DO, mg/L	Eh, mV	pH	Parameters and metals
Case of high Eh									
								1	pH
							1	0.215	Eh, mV
						1	0.813	0.283	DO, mg/L
					1	0.042	0.022	0.580	EC, µs/cm
				1	1	0.042	0.022	0.580	TDS, mg/L
			1	0.256	0.256	-0.525	-0.610	-0.008	Fe, µg/L
		1	0.908	0.534	0.534	-0.467	-0.591	0.121	Mn, µg/L
	1	0.870	0.836	0.159	0.159	-0.706	-0.759	-0.074	Pb, µg/L
1	-0.205	-0.410	-0.172	-0.728	-0.728	0.230	0.162	-0.525	Zn, µg/L
Case of low Eh									
								1	pH
							1	0.650	Eh, mV
						1	0.863	0.592	DO, mg/L
					1	-0.078	-0.134	0.601	EC, µs/cm
				1	1	-0.078	-0.134	0.601	TDS, mg/L
			1	-0.191	-0.191	-0.686	-0.752	-0.672	Fe, µg/L
		1	0.448	0.550	0.550	-0.753	-0.718	-0.054	Mn, µg/L
	1	0.427	0.943	-0.295	-0.295	-0.711	-0.681	-0.691	Pb, µg/L
1	-0.409	-0.463	-0.439	0.242	0.242	0.656	0.570	0.499	Zn, µg/L

Regression equations were calculated from the pairs of variables to understand the hydrochemistry of treated runoff. The regression coefficients, equations and the R-Square values are depicted in **Table 3**. The higher the value of R-Square, the better is the proper and more useful the regression parameters [13]. The significance of the regression equations was shown by p-value ($p < 0.05$).

It was evident that during high Eh, EC and Eh were the most appropriate variables predicting more than 66% and 100% of DO and TDS, respectively. Fe and Mn were the most appropriate variables predicting more than 82%, 70%, and 75% of Mn and Pb respectively. The R-Square values suggested that the examined variables had a strong association. The p-values of the DO-Eh, TDS-EC, Mn-Fe, Pb-Fe, and Pb-Mn equations were: 0.00121, 0.00000, 0.00000, 0.00069, 0.00023 ($p < 0.05$), respectively. This significantly explained the adequacy of the models for predicting how the metals and runoff quality parameters affected each other after PEC treatment during high Eh. While during low Eh, EC, Eh, and Fe were the most appropriate variables predicting more than 74%, 100%, and 88% of DO, TDS, and Pb, respectively. The p-values of the DO-Eh, TDS-EC, and Pb-Fe equations were: 0.00030, 0.00000, and 0.00000 ($p < 0.05$), respectively.

To calculate the percentage contribution of an independent variable to a dependent variable, a maximum value of a dependent variable (y) in the linear regression equations depicted in **Table 3** was considered, an independent variable (x), as well as its percentage contribution to y, was calculated.

Based on the data in **Table 3** and during high Eh, it appeared that the highest percentage contribution to TDS was by EC (99.70%), and this result proposed a dominance of EC in the control of TDS. The known values of EC, TDS, and Fe contribution to Mn were 33.00%, 21.00%, and 45.60%, respectively, Fe and Mn to Pb showed 95.00% and 5.00% contribution, respectively. While in the case of low Eh, the highest contribution to DO was by Eh (94.13%), to TDS was by EC (99.74%), to Mn was by Fe (69.20%), and to Zn was by Eh (93.37%). Many calculated contributions were found to match the R-Square values obtained from models, indicating that the regression models were accurate. For example, according to the calculated contributions (99.70%, 0.29%) and R-Square values (100%, 33%) of TDS-EC and TDS-pH, respectively, it was concluded that the contribution of EC to TDS was higher than pH to TDS during high Eh.

Table 3. Linear regression equations of different metals and physicochemical parameters

Dependent variable (y)	Independent variable (x)	Correlation coefficient (r)	Regression equations y = ax + b	R Square	*p*-value	% Calculated contribution x to y
			The case of high Eh			
DO	Eh	0.813	DO = -2.9712 + 0.0384 Eh	0.66	0.00121*	-
EC	pH	0.580	EC = -12408.8000 +1851.5300 pH	0.33	0.04800**	-
TDS	pH	0.580	TDS = -7941.6000 + 1184.9800 pH	0.33	0.04800**	0.29
TDS	EC	1	TDS = 0.6400 EC	1.00	0.00000*	99.70
Mn	EC	0.534	Mn = -7.9389 + 0.0683 EC	0.28	0.07200***	33.00
Mn	TDS	0.534	Mn = -7.9389 + 0.1067 TDS	0.28	0.07200***	21.00
Mn	Fe	0.908	Mn = 49.5330 + 0.0421 Fe	0.82	0.00000*	45.60
Pb	Fe	0.836	Pb = 2.3690 + 0.0007 Fe	0.70	0.00069*	95.00
Pb	Mn	0.870	Pb = 1.6169 + 0.0160 Mn	0.75	0.00023*	5.00
			The case of low Eh			
Eh	pH	0.650	Eh = -228.7750 + 40.1500 pH	0.42	0.02200**	-
DO	pH	0.592	DO = 0.2603 +0.5320 pH	0.35	0.04200**	5.85
DO	Eh	0.863	DO = 3.3110 + 0.0125 Eh	0.74	0.00030*	94.13
EC	pH	0.601	EC = -1673.1600 + 559.6400 pH	0.36	0.03800**	-
TDS	pH	0.601	TDS = -1070.8200 + 358.1700 pH	0.36	0.03800**	0.25
TDS	EC	1	TDS = 0.6400 EC	1.00	0.00000*	99.74
Mn	EC	0.550	Mn = 399.1560 + 0.0910 EC	0.30	0.06300***	18.80
Mn	TDS	0.550	Mn = 399.1560 + 0.1428 TDS	0.30	0.06300***	11.98
Mn	Fe	0.448	Mn = 376.8200 + 0.0258 Fe	0.20	0.14300	69.20
Pb	Fe	0.943	Pb = 7.7150 +0.0025 Fe	0.88	0.00000*	-
Zn	pH	0.499	Zn = -14.0790 + 6.6460 pH	0.25	0.09900***	4.00
Zn	Eh	0.570	Zn = 24.9550 + 0.1229 Eh	0.32	0.05000**	93.37
Zn	DO	0.656	Zn = -7.2450 + 9.7310 DO	0.43	0.02040**	2.50

Note: * indicates significance at the 1% level, ** indicates significance at 5% level and ***indicates significance at the 10% level.

Accordion to the regression equations, for each unit increase in Eh, DO increased at least 0.0384 in the treated runoff during aerobic conditions. This was in agreement with the finding by M.S. Muñoz *et al.* [21], who observed that the positive values of Eh in runoff were because of abundant DO. In aerobic and anaerobic conditions, for each unit increase in pH in the treated runoff, EC increased at least 1851.5300 and 358.1700, respectively. This result confirmed the finding obtained by D. de Paiva Magalhães *et al.* [22] who reported that the ionic strength (EC), which is the measurement of free ions in solution, increased with increasing the salts of carbonate and bicarbonate and hydroxyl ions, which is measuring as pH.

The slopes of the three Mn-Fe, DO-Eh, and Pb- Fe linear regression equations, which were 0.0421, 0.0384, and 0.0007 in the high Eh conditions and 0.0258, 0.0125, and 0.0025 in the low Eh conditions, were different. The different relationships displayed by Mn- Fe, DO-Eh, and Pb-Fe were thought to be due to the differences in the speciation of these metals and these parameters in the two conditions of treatment.

Conclusion

For the first time, the current study assessed the correlation between the metals according to Eh/pH diagrams in treated Tehran runoff. Only Zn affected the removal of Fe during PEC treatment. Multiple regression analysis showed no significant relationship between the PEC removal of COD and studied metals; these metals were invalid indicators and cannot be suitable predictors of COD after treatment in the case of high Eh. However, in the case of low Eh, Mn was proved to be a good predictive parameter of the residual COD. By analyzing Eh, EC, Fe, and Mn, the concentration of the better-related variables DO, TDS, Mn, and Pb after treatment could be estimated. Such studies can be facilitated using the new multi-metals HSC approach without needing the surface analysis laboratory techniques (AFM, XRD….), and using the regression equations without needing to measure COD after the PEC process during low Eh or measure all metals and parameters during all cases of treatment. This study provided information on the treated runoff quality by PEC process and it would serve as a database for further investigations.

Acknowledgement

The present research was sponsored by Ministry of Higher Education and Al-Baath university, Syria. We also thank University of Tehran for providing us with the electro-flocculation laboratory to carry out the analysis.

Disclosure statement: *Conflict of Interest:* The authors declare that there are no conflicts of interest.

Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

Declaration

Funding

Not applicaple**.** The authors did not receive support from any organization for the submitted work.

No funding was received to assist with the preparation of this manuscript.

CONFLICTS OF INTEREST/COMPETING INTERESTS

The authors declare that there is not any conflict of interest regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

AVAILABILITY OF DATA AND MATERIAL

The data used to support the results of this research are available from the corresponding author upon request

CODE AVAILABILITY

Not applicable

AUTHORS CONTRIBUTIONS

Gh. conducted the literature review, planned the experimental design, and analyzed and interpreted the information, in addition to writing the manuscript. A.R. and N. supervised and helped in the literature review and the manuscript preparation.

Ethics approval and consent to participate

All authors agree to participate

Consent for publication

All authors agree to the publication

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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